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STRUCTURAL INTERPRETATION OF CONCENTRATION DEPENDENCES OF MOLAR VOLUME OF GLASSES IN $R_2O - SiO_2$ AND $RO - SiO_2$ SYSTEMS

A. I. Rabukhin¹

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A method is considered for structural interpretation of concentration dependences of properties of binary silicate glasses (with the example of glass molar volume) based on establishing a correlation between the values of a certain property and the degree of depolymerization of the silicon-oxygen skeleton (structural lattice) of glass R^* which reflects the number of non-bridge oxygen ions per silicon-oxygen tetrahedron. Partial values of molar volumes are determined for a series of oxides of the first and second groups of the periodic system, which preserve their constant values over the entire glass-formation area. The estimate error in calculating the molar volume of glasses according to the proposed method is around 1%.

The known methods for estimating properties of silicate glasses (for example, according to Appen or Demkina) imply the determination of partial values of oxides by extrapolation of experimental data on glass properties or interpolation of increments in property values caused by adding a certain component. Data processing based on these methods produces variables (for example, for SiO_2 or PbO) depending on glass composition, values of the properties of components [1], or a discrete set of such values [2 – 4]. To account for these facts, Appen considers variations in the structural state of such components following the variation in the glass composition, and Demkina introduces the notion of “property fields” correlating with the phase fields (primary crystallization fields) of phase diagrams, which has no strict physicochemical meaning for nonequilibrium single-phase vitreous systems [5]. These circumstances decrease the reliability of structural interpretation of concentration dependences of glass properties.

Another approach to describing silicate glass properties [6, 7], which implies the presence of certain chemical compounds in glass, is rather formal as well, since the true composition, structure, and concentration of chemical compounds in glasses are unknown.

The present paper considers the method of structural interpretation of concentration dependences of silicate glass properties (with the example of molar volume of glasses), which is based on establishing a correlation between the values of a particular property and the degree of depolymerization of the silicon-oxygen skeleton (structural lattice) of

glass R^* , which reflects the number of non-bridge oxygen ions per silicon-oxygen tetrahedron.

According to the existing concepts [8], the quartz-glass structural lattice is constructed from silicon-oxygen polyhedrons (tetrahedrons), in whose centers Si^{4+} ions are located. The silicon-oxygen tetrahedrons are bonded by apexes occupied by what is known as oxygen bridge ions, as a consequence of which the continuous glass-forming skeleton is formed, in which the tetrahedrons are bonded by bridge bonds – $Si - O - Si -$. When modified oxides R_2O and (or) RO are introduced into purely silica glass, the glass-forming skeleton becomes depolymerized due to the rupture of bonds – $Si - O - Si -$ and, consequently, emergence of non-bridge oxygen ions. The modifying oxide ions are located in the emerging ruptures of the structural lattice, thus compensating for its excessive negative charge caused by the presence of non-bridge oxygen ions.

According to Stevels [9], the degree of bondedness of the structural lattice of silicate glass is determined by the ratio $R = O : Si$ reflecting the average number of oxygen ions per cation incorporated in the structural lattice (in this case, per cation of Si^{4+}). Thus, for pure silica glass $R = 2$, for metasilicate glass ($R_2O \cdot SiO_2$ or $RO \cdot SiO_2$) $R = 3$, and when the modifying oxide concentration increases to a value corresponding to orthosilicate ($2R_2O \cdot SiO_2$, $2RO \cdot SiO_2$), the level of $R = 4$ is attained.

The number of nonbridge oxygen ions X per silicon-oxygen tetrahedron in the specified series of compositions varies in the following way:

SiO_2 — all four oxygen ions are bridge ions and take part in constructing a continuous three-dimensional skeleton; ac-

¹ D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

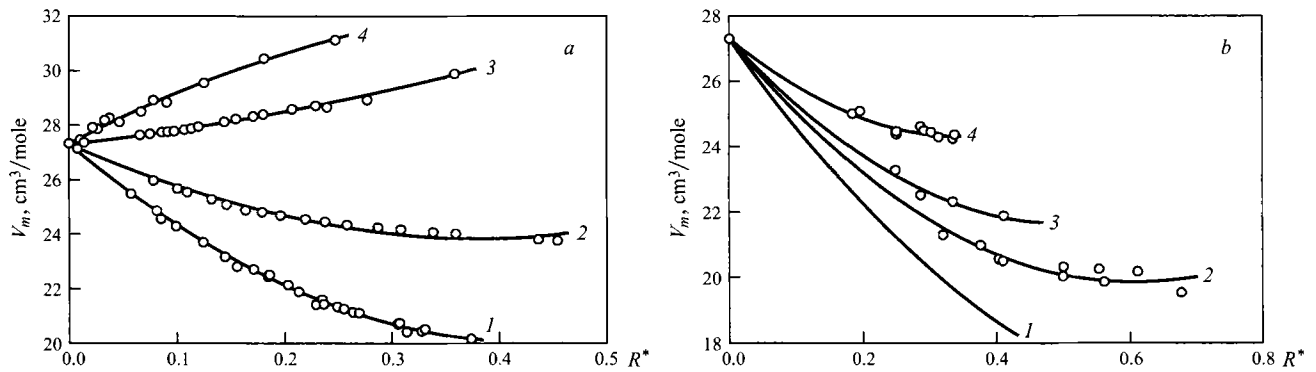


Fig. 1. Concentration dependence of molar volume of glasses in $R_2O - SiO_2$ (a) and $RO - SiO_2$ (b) systems. R_2O : Li_2O (1), Na_2O (2), K_2O (3), Rb_2O (4); RO : MgO (1), CaO (2), SrO (3), BaO (4). Solid lines) estimated values; dots) experimental values given by various authors (Table 1).

cordingly, $X = 0$, and the depolymerization degree of the skeleton $R^* = 0$;

metasilicate — only two bridge oxygen ions can take part in the formation of unidimensional (chain) structures and, accordingly, the depolymerization degree of the structural lattice increases to $R^* = 0.5$ (up to 50%);

orthosilicate — formation of branched spatial systems is impossible, since all four oxygen ions are non-bridge ions,

and accordingly, the depolymerization degree of the structural lattice attains the value $R^* = 1$ (i.e., 100%).

The linear approximation of the specified values of the structural lattice depolymerization degree for silicate glasses R^* and the parameter R produces the equation

$$R^* = (R - 2)/2.$$

Since the dependence of the parameter R on the modifying oxide concentration x (x is the molar part of the modifying oxide) is determined from the expression

$$R = (x + 2(1 - x))/(1 - x) = (2 - x)/(1 - x),$$

we have

$$R^* = x/(2(1 - x)). \quad (1)$$

The molar volume of glasses ($cm^3/mole$) was calculated by the generally known formula [1]

$$V_m = M_m/\rho = (m_m x + 60.06(1 - x))/\rho,$$

where M_m is the molar mass of glass, $g/mole$, ρ is the glass density, g/cm^3 , m_m and 60.06 are the molar masses of the modifying oxide and SiO_2 , g , and x is the content of the modifying oxide, molar parts.

The authors analyzed the type of dependence of molar volume on the depolymerization degree of the structural lattice of binary silicate glasses for systems $R_2O - SiO_2$ ($R_2O - Li_2O$, Na_2O , K_2O , Rb_2O) and $RO - SiO_2$ ($RO - MgO$, CaO , SrO , BaO) using experimental data on the density of specified glasses supplied by various authors.

It was found that the dependence of V_m on R^* of the considered glasses can be approximated with a high degree of precision (Table 1, Fig. 1) by the equation

$$V_m = 27.29 + k_{1j}R^* + k_{2j}R^{*2}, \quad (2)$$

where 27.29 is the molar volume of vitreous silica calculated on the basis of the value $\rho = 2.202 \text{ g/cm}^3$ (the averaged

TABLE 1

System*	Relative mean quadratic error of V_m calculation, %	Number of glass compositions used in data processing	Reference
$Li_2O - SiO_2$	0.41	25	[10**, 11]
$Na_2O - SiO_2$	0.47	17	[10**]
$K_2O - SiO_2$	0.18	47	[10**, 12]
$Rb_2O - SiO_2$	0.48	14	[10]
$CaO - SiO_2$	1.15	10	[10, 13]
$SrO - SiO_2$	0.61	4	[10, 13]
$BaO - SiO_2$	0.50	10	[10]

* Due to the absence of published data on density, the V_m calculation error for the $MgO - SiO_2$ system was not determined.

** Glass composition was derived from analysis.

TABLE 2

Modifying oxide	k_{1j}	k_{2j}
Li_2O	-33.9	39.4
Na_2O	-17.74	22.64
K_2O	4.54	7.54
Rb_2O	21.44	-22.04
MgO^*	-29.0	18.6
CaO	-24.5	20.3
SrO	-22.3	22.0
BaO	-16.9	23.9

* Values of k_{1j} for MgO were obtained by linear extrapolation of the data shown in Fig. 2.

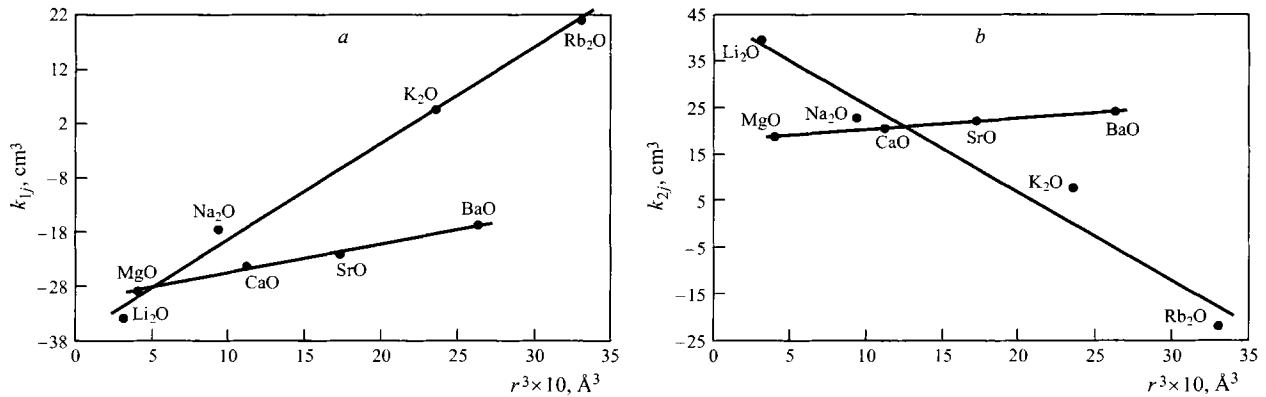


Fig. 2. Dependence of partial coefficients k_{1j} (a) and k_{2j} (b) on the cube of the radius of modifying oxide cation in glasses (values of cation radii are given according to data in [14]).

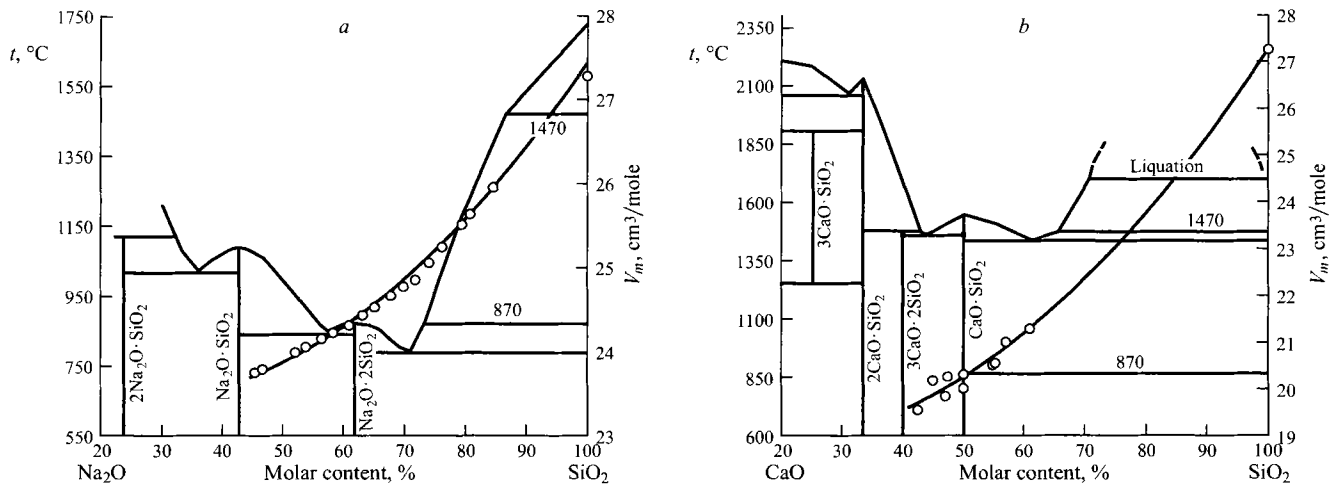


Fig. 3. Correlation of the type of concentration dependence of glass molar volume in systems $\text{Na}_2\text{O}-\text{SiO}_2$ (a) and $\text{CaO}-\text{SiO}_2$ (b) with structural specifics of respective phase diagrams. Solid lines) estimated values of molar volume; dots) experimental values given by various authors (Table 1).

value found in [10]), and k_{1j} and k_{2j} are partial coefficients of modifying oxides (Table 2).

The linear correlation existing between the values k_{1j} , k_{2j} , and the cubic radius of the modifying oxide cation (Fig. 2) can be expressed by the following equations:

for R_2O :

$$k_{1j} = -37.3 + 17.8r_j^3; \quad (3)$$

$$k_{2j} = 44.4 - 18.8r_j^3; \quad (4)$$

for RO :

$$k_{1j} = -31.0 + 5.3r_j^3; \quad (5)$$

$$k_{2j} = 17.6 + 2.4r_j^3. \quad (6)$$

These data indicate that the modifications occurring to the glass structural lattice in depolymerization (i.e., as the concen-

tration of the modifying oxide increases; see Eq. (1)), which are accompanied by the modifier cations filling the breaks in the structural lattice, are determined by two opposite factors: either consolidation of the structural lattice (decrease in V_m) or loosening of the lattice (increase in V_m).

The contribution of the k_{1j} factor to the estimated value V_m is usually negative (consolidation of the lattice, i.e., a decrease in V_m , see Eq. (2)), but with increasing values of r , this effect becomes weaker (see Eqs. (3) and (4)); for example, in the case of K_2O and Rb_2O the values of k_{1j} become positive (Table 2 and Fig. 2), i.e., loosening of the structural lattice is registered.

In the analysis of the contribution of the factor k_{2j} to the value V_m it should be taken into account that R^{*2} is the cofactor of k_{2j} in Eq. (2). Since the value R^* is of the order of a fraction of unity, with $R^* < 1$ the value R^{*2} will always be less than R^* . For example, for $R^* = 0.6$, $R^{*2} = 0.36$. Accordingly, the contribution of the coefficient k_{2j} to the value V_m is

usually lower than in the case of the coefficient k_{ij} and can be regarded as a secondary effect.

However, it should be noted that the contribution of the coefficient k_{2j} to the estimated value V_m is usually positive (Eqs. (4) and (6)) and results in loosening of the lattice (an increase in V_m , Eq. (2)). With increasing values of r in alkaline modifier oxides, this effect becomes weaker (Eq. (4)) and, for instance, in the case of Rb_2O the value of k_{2j} can even become negative (Table 2 and Fig. 2). With increasing values r of modifying cations R^{2+} , the loosening effect of the increment related to coefficient k_{2j} monotonically increases (Eq. (6)).

As the result, the observed general tendency of the concentration dependences of molar volume of the considered binary silicate glasses in $\text{R}_2\text{O} - \text{SiO}_2$ and $\text{RO} - \text{SiO}_2$ systems indicates that the structural lattice of these glasses as a rule becomes consolidated in the course of its depolymerization (Fig. 1). The exceptions to this general rule are potassium- and rubidium-bearing glasses, which exhibit loosening of their structural lattices as their depolymerization increases.

Since the approximation of concentration dependences of silicate-glass properties is performed in some publications [2–4] using fractional-linear functions correlated with phase-diagram fields, we have correlated the concentration dependences of the molar volume of binary silicate glasses (with the example of glasses in the $\text{Na}_2\text{O} - \text{SiO}_2$ and $\text{CaO} - \text{SiO}_2$ systems) with the structural specifics of the respective phase diagrams.

It was found (Fig. 3) that the specified concentration dependences have a smooth monotonic shape and do not exhibit sharp deviations in the transition via phase-field boundaries in the phase diagrams considered. This completely agrees with the conclusions in [15] and indicates that the reasoning given in [2–4] is rather formal.

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